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CITATION:

Yamada, Takeshi ...[et al]. 25. Effect of Li ions on micro-phase separated structure of amphiphiilc di-block copolymer(poster presentation,Soft Matter as Structured Materials). 物性研究 2005, 84(6): 911-912

ISSUE DATE:

2005-09-20

URL:

http://hdl.handle.net/2433/110304

Effect of Li ions on micro-phase separated structure of amphiphiilc di-block copolymer

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【要旨】

我々は PEO-*b*-PMA(Az) ブロック共重合体が、高秩序なヘキサゴナルシリンダー構造を形成することを報告してきた。本研究では、PEO-*b*-PMA(Az) ブロック共重合体に $LiCF_3SO_3$ を添加したときの影響について、小角 X 線散乱 (SAXS) と DSC 測定を用いて検討した。$LiCF_3SO_3$ の添加濃度が低い時は、PEO ドメインと PMA(Az) ドメイン間の電子密度差を増大させ、添加濃度が高い時は、$LiCF_3SO_3$ が PMA(Az) ドメインの液晶構造の秩序性を低下させ、ミクロ相分離構造の秩序性が低下することが明らかになった。

Introduction

Recently we have reported micro-phase separated structures and phase transitions of the amphiphilic di-block copolymer (PEO_m-*b*-$PMA(Az)_n$) which consisted of hydrophilic poly ethylene oxide (PEO) and hydrophobic poly methacrylate derivatives having azobenzene moieties (PMA(Az)). PEO-*b*-PMA(Az) di-block copolymers form highly nano-sacale ordered hexagonal packed PEO cylinder structure in a single domain with $1\mu m^2$[1,2]. These highly ordered nano-scale structure expected to used as anisotropic electron conductive devices. In this study, effects of Li-salts to micro-phase structure of PEO-*b*-PMA(Az) di-blcok copolymer were investigated by SAXS and DSC measurements.

Samples and Experiments

PEO_m-*b*-$PMA(Az)_n$/salt mixtures were prepared by dissolving PEO_{40}-*b*-$PMA(Az)_{44}$ and $LiCF_3SO_3$ in THF. The $LiCF_3SO_3$ concentration was from 1 to 120 (EO/Li^+). After removing solvents, samples were annealed at 150 °C in vacuum oven for 24 hr. SAXS measurements were performed at several temperatures by BL-10C (KEK, PF). The wavelength of X-ray was 0.1488nm. The q range was $0.1 < q = 4\pi \sin\theta / \lambda < 3$ nm^{-1}. DSC measurements were performed by DSC 6200 (Seiko Instrument Inc.) equipped with cooling apparatus in the temperature range between -50 and 200 °C. Scanning rate was 10 K min^{-1} in a flowing nitrogen atmosphere (40 ml min^{-1})

Results and Discussions

PEO_{40}-*b*-$PMA(Az)_n$ formed a highly ordered hexagonal packed PEO cylinder structure by TEM observation (Fig.1), however no SAXS peaks were observed as shown in Fig.2.

SAXS profiles of PEO_{40}-*b*-$PMA(Az)_{44}$/ $LiCF_3SO_3$ systems were shown in Fig.2. The peaks assigned to the hexagonal cylinder structure were appeared by addition of Li -salts. The addition of Li-salts enhanced the electron density difference between PEO and PMA(Az) domains. Below EO/Li^+ = 8, the peak width expanded and the (100) plane distance increased with the increase of Li-salt amount.

Transition temperature and entropy of the isotropic transition of PMA(Az) domain were shown in Fig.3. As the transition temperature and entropy were the same as the case of no salts above EO/Li^+ = 20, the salt had no effect to the PMA(Az) domain and was expected to exist in PEO domain. In the case of EO/Li^+ = 8 and 4, the transition entropy was less than the case of no salts and the SAXS peak width of LC structure (q = 2 nm^{-1}) was wider than no salts. This result indicated that the disordering of the LC phase structure was induced by the salt existing in not only the PEO domain but also the PMA(Az) domain. In the case of EO/Li^+ = 1, the thickness of the smectic LC phase increased. The transition temperature and entropy widely changed. It seems that the LC phase structure of EO/Li^+ = 1 was different from others.

These results sugested that $LiCF_3SO_3$ enhanced the electron density difference in low concentration region and affected both the nano-sacale ordered structure and LC phase structure in high concentration region.

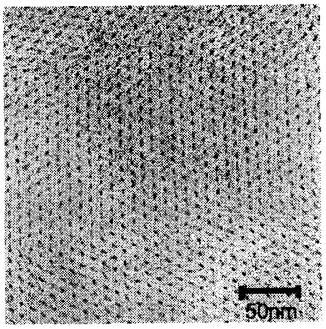

Fig.1: TEM image of PEO_{44}-*b*-$PMA(Az)_{24}$.

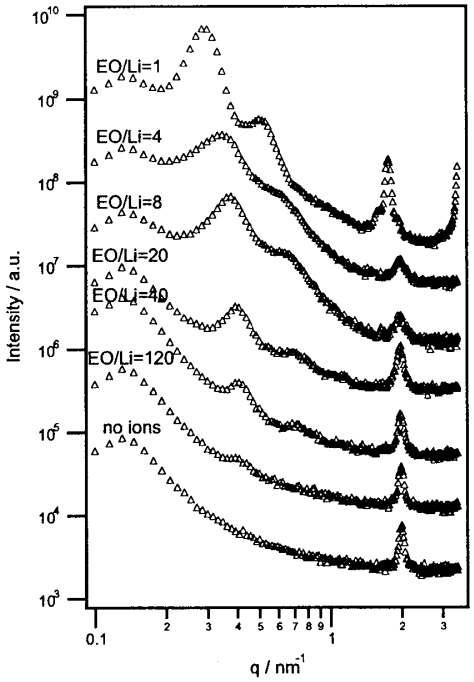

Fig.3: SAXS profiles of PEO_{44}-*b*-$PMA(Az)_{44}$ / $LiCF_3SO_3$ systems.

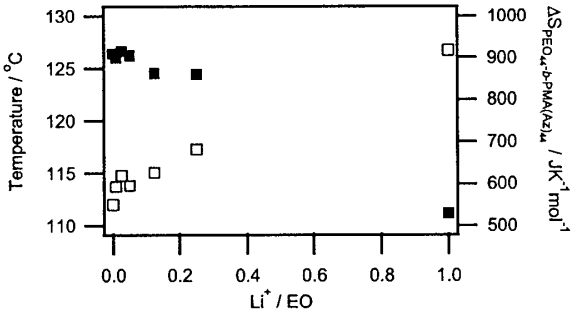

Fig.3: Transition temperature (unfilled) and entropy of the isotropic transition (filled).

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